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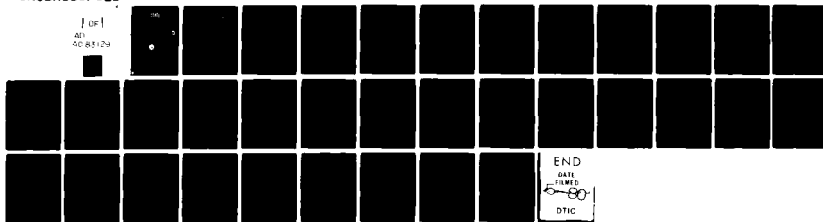
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HEAT STABLE POLYMERS:
POLYQUINOLINES AND
OTHER AROMATIC POLYMERS

Final Report

J. K. Stille

January 1977-December 1979

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Polyquinolines can be synthesized by an acid catalyzed polymerization reaction that allows a variety of structural modifications, resulting in a range of chain stiffness that can be altered from a relatively flexible amorphous polymer with a moderately low glass transition temperature (250°C) to a rod-like molecule with a high degree of crystallinity and a high crystalline transition temperature (>550°C). Fibers can be spun and films cast from solution. The rigid rod polyquinolines form anisotropic solutions | | |

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and, as a result, produce crystalline fibers with a high degree of orientation and a high modulus.

A series of polyquinolines containing biphenylene units in the main chain were prepared in order to effect crosslinking reactions of these materials. Crosslinking took place thermally, above the Tg of the polymer, to give insoluble polymers with higher Tg's and higher moduli both above and below Tg. Transition metals catalyze the crosslinking reactions, allowing lower curing temperatures. Polyaramides, polybenzimidazoles and polyquinoxalines could be similarly crosslinked by incorporating biphenylene into these polymers.

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INTRODUCTION

Linear rigid chain macromolecules generally exhibit greater mechanical strength and higher phase transition temperatures than the more flexible chain polymers. Such materials, for example, are fabricated into composites or laminates for use in helmets, helicopter blades, vehicle cabs, rockets, and recoilless rifles where high strength is gained from a high modulus fiber in a matrix, both of which are polyaromatics.¹ High modulus fibers also find use in body armor and high temperature electrical insulation.

Most of the polymers with highly rigid recurring units in the chain, however, are either crystalline, or have high melting (softening) temperatures and are insoluble in suitable solvents as a result of ring (particularly aromatic ring), spiro, or ladder structures in the main chain. One of the major unsolved problems is in the fabrication of such materials having high use temperatures.

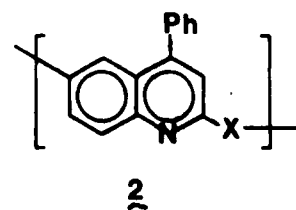
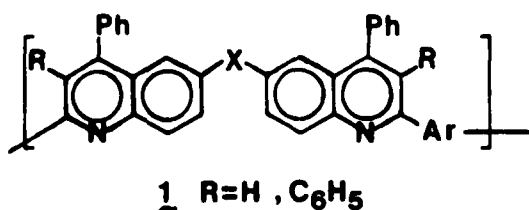
A polymer with a high use temperature is defined by two variables of thermal performance: 1) A threshold temperature at which the polymer loses its mechanical strength under an external applied load of specific magnitude. 2) A threshold temperature corresponding to the occurrence of chemical changes in the structure of the polymer accompanied by corresponding changes in properties. The first variable requires a material with a high glass transition temperature, a high crystalline temperature combined with a relatively high degree of crystallinity, or a three dimensional network structure. In order to achieve melt processability, the synthesis of an uncross-linked material with relatively low transition temperatures is necessary. Subsequently these transition temperatures can be raised by some chemical means after processing to give a more rigid chain or a three-dimensional network structure. An alternate approach to this problem is to

process the polymer in the amorphous state in which a moderately high glass transition temperature (e.g. 250°C) is obtained, and then develop crystallinity during processing or subsequent annealing to raise the use temperature (e.g. $T_m = 450-550^\circ\text{C}$) to the limit of thermal performance as defined by the second variable.

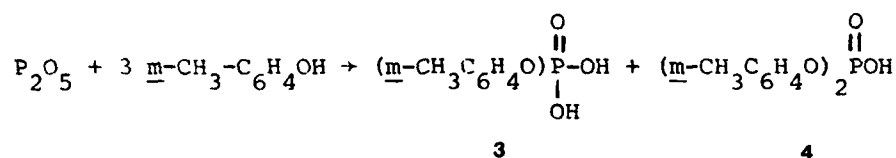
POLYQUINOLINES

Background.

Thermally stable polymers containing quinoline units in the chain can be synthesized by a polymerization reaction that allows a variety of structural modifications, resulting in a range of chain stiffness that can be altered from a relatively flexible polymer with a low glass transition temperature to a rod-like molecule with a high glass transition temperature.²⁻⁷ Most of the materials have high crystalline transition temperatures, but a low degree of crystallinity. For example, polyquinolines **1** ($X=O$, $\text{Ar}=4,4'\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4$) containing some flexibility, exhibit lower transition temperatures ($T_g=265-350$, $T_m=450-480$) and lower crystallinity (<20%) than the rigid polyquinoline **2** ($X=\text{nil}$, $p\text{-C}_6\text{H}_4$; $T_g=380-415$, $T_m=552-580$). The largely amorphous polyquinolines, of which **1** is representative, are characterized by high moduli below the glass transition temperature ($E' = 6 \times 10^{10}$ dynes/cm², **1**, $R=\text{H}$, $X=O$, $\text{Ar}=4,4'\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4$), and good solubility in common organic solvents. In addition, all polyquinolines show excellent thermal stability as determined by thermal gravimetric analysis and isothermal ageing.



The polymerization reaction of an aromatic bis-o-aminoketone with an aromatic bisketomethylene monomer has been shown to give high molecular weight polyquinoline by acid catalysis. The reaction is first order in aminoketone concentration and first order in ketomethylene concentration. Optimum polymerization rates and molecular weights were obtained in mixtures of m-cresol and the reaction product of m-cresol and phosphorus pentoxide. The reaction product was shown^{8,9} by ³¹P nmr to consist of an equimolar mixture of mono-(3) and di-m-cresol (4) esters of phosphoric acid, as the stoichiometry suggests.



Both esters, **3** and **4** were independently synthesized, and although mixtures of ester **3** and m-cresol were marginally effective as a polymerization medium, ester **4** with m-cresol effected the polymerization at about the same rate as the m-cresol phosphorous pentoxide reaction mixture. One added advantage of the independently synthesized (and purified) diester **4** is that much higher molecular weights could be obtained. The upper degree of polymerization attainable in the phosphorus pentoxide m-cresol reaction mixture appears to be about 320, possibly as a result of some side reaction with one or more of the monomer functional groups. Acid catalyzed cyclotrimerization has been suggested⁴ as a reaction which would not only consume ketomethylene groups, but also would lead to branching. Polymerization in a mixture of m-cresol and **4**, however, gives a DP>550 in 24 h.

In most cases, the processability of thermally stable polymers is limited by insolubility and high phase transition temperatures. A soluble

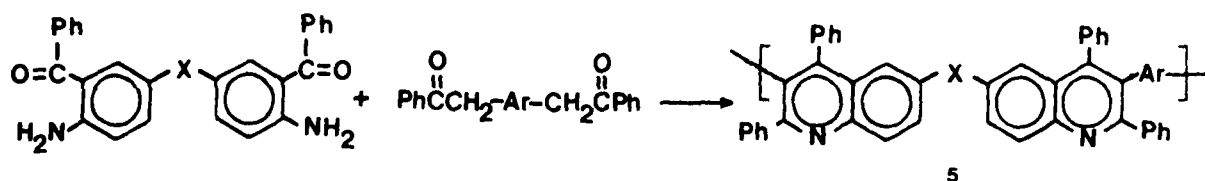
polyaromatic is often amorphous and has a relatively low glass transition temperature. If the T_g or T_m of thermally stable amorphous or crystalline polyaromatics are low such that they can be processed by melt techniques, then their use temperature is low, limited by T_g or T_m .

Polyquinolines of the general structure 1 ($x=O$) are largely amorphous and have glass transition temperatures of 350°C or lower. Thus, although they are soluble in common organic solvents, and can be readily fabricated from solution, their use temperature is limited to 350°C or lower. The use temperature cannot be raised to the crystalline transition temperatures since annealing does not develop sufficient crystallinity.

Polyquinolines 2 ($x=\text{nil}$, $p\text{-C}_6\text{H}_4$) are sufficiently crystalline and have high enough crystalline transition temperatures, 480°C and 580°C , respectively, but are soluble only in strong acids such as sulfuric acid. The storage moduli of each one is also sufficiently high, ($E' \approx 4 \times 10^{10}$ dyn/cm² even above their glass transition temperatures ($E' \approx 2.5 \times 10^{10}$ dyn/cm² such that good mechanical properties are retained up to T_m .

Polymers Containing 3,6-Quinoline Units¹⁰

In an effort to prepare polyquinolines which would have good solubilities and show the ability to crystallize by annealing above the T_g , polymers containing 3,6-quinoline units in the main chain were synthesized. These polymers can be prepared by the condensation of bis-o-amino ketones with bis-phenacyl monomers in place of the bis-phenylacetyl monomers. Thus, the synthesis of a number of new bis-phenacyl monomers was accomplished.









These polymers (5) showed improved solubilities over the analagous polyquinolines with the 2,2'-catenation, being readily soluble in chloroform or sym-tetrachloroethane (TCE). Tough, transparent films of 5a-c could be cast from 10-15% by wt. solutions of the polymers in chloroform, TCE or m-cresol. When preparation of a 10-15% by wt. solution of 5c in chloroform was attempted, the polymer initially went into solution, but then slowly precipitated. The solvent was allowed to evaporate slowly and the resultant thick opaque film was analyzed for crystallinity. From x-ray analysis, the film was estimated to be approximately 50 percent crystalline, exhibiting very light diffuse halos due to amorphous regions at 9.0 and 4.9 Å and numerous sharp diffraction lines due to crystalline regions the most intense of which were at 11.4, 8.7, 5.0, 4.5 and 4.0 Å. Thus, polymer 5c could be crystallized to a moderately high degree from a chloroform solution.

Polymers 5d,f exhibited good solubilities in m-cresol, whereas, 5e exhibited only limited solubility in concentrated sulfuric acid. Films of 5d,f could be cast from 10% wt. solutions of the polymers in m-cresol. A film of 5e could not be obtained due to the polymer's poor solubility.

Pressed powder and film samples of polyquinolines (5) were analyzed by differential scanning calorimetry (DSC) and by dynamic thermomechanical analysis to obtain information on thermal transitions that occur in the polymers (Table 1). The glass transition temperatures (T_g) ranged from 255 to 390°C, with polymers 5d-f having T_g's 50-65°C higher than the more flexible polymers 5a-c.

Polymers 5d-e exhibited crystalline transition temperatures (T_m) ranging from 475-530°C, whereas, polymers 5a-c did not exhibit crystalline transitions. This difference in crystallinity of the polymers apparently is due,

TABLE I
Properties of 3,6-Polyquinolines

| Polymer | X | Ar | Solubility ^a | [n] (solvent) dl/g | DSC | E"max | T _c (°C) | T _m (°C) | Thermal Stability | | |
|---------|-----|---|--------------------------------|--------------------------------------|-----|-------|---------------------|---------------------|-------------------|---------|------------------------|
| | | | | | | | | | Air Break | Break % | Nitrogen loss at 800°C |
| 5a | O |  | CHCl ₃ | 1.2(CHCl ₃) | 255 | 250 | - | - | 530 | 575 | 30 |
| 5b | O |  | CHCl ₃ | 0.7(CHCl ₃) | 312 | 310 | - | - | 535 | 570 | 28 |
| 5c | O |  | TCE ^b | 3.6(<u>m</u> -cresol) | 325 | 335 | - | - | 530 | 550 | 28 |
| 5d | nil |  | <u>m</u> -cresol | 0.8(<u>m</u> -cresol) | 305 | 310 | 415 | 475 | 575 | 580 | 30 |
| 5e | nil |  | H ₂ SO ₄ | 0.5(H ₂ SO ₄) | 370 | - | 437 | 550 | 570 | 575 | 25 |
| 5f | nil |  | <u>m</u> -cresol | 2.4(<u>m</u> -cresol) | 390 | 420 | - | 530 | 570 | 585 | 25 |

a. Solubility defined as the ability to dissolve 10% by wt. of polymer

b. sym-tetrachloroethane

at least to some extent, to the variation in the rigidity of the polymer chains, since rigid polymers generally exhibit a higher degree of crystallinity than flexible polymers. The difference in the amount of crystallinity is apparently small though, since both types of polymers 5a-c and 5d-f are essentially x-ray amorphous (<20% crystalline).

In addition to high crystalline transition temperatures, polymers 5d,e showed crystallization temperatures (T_c) of 415 and 437°C. When polymers 5c and 5e were annealed at their respective T_c 's for one hour and then slowly cooled and the DSC scan was run again, the magnitude of the T_g had decreased and the exotherm corresponding to the T_c was no longer observed. The continued presence of the T_g indicates that the polymers still have amorphous regions which did not crystallize on annealing.

Dynamic thermomechanical analysis showed that polymer 5d exhibited only a small loss of modulus at its T_g , indicative of the presence of a considerable amount of crystallinity in the polymer. When 5c was annealed at 440°C, within 15 min., the storage modulus had increased 2.6×10^8 to 1.1×10^{10} dynes/cm², as a result of an increase in crystallinity to approximately 30 percent.

As expected, the polyquinolines synthesized in this work showed outstanding thermal stability both in inert atmospheres as well as in air (Table 1). Thermogravimetric analysis (TGA) of the polymers showed breaks in air at 530-570°C, with breaks in nitrogen at 550-585°C and only 25-30% weight loss at 800°C under nitrogen.

Cardo Polyquinolines.

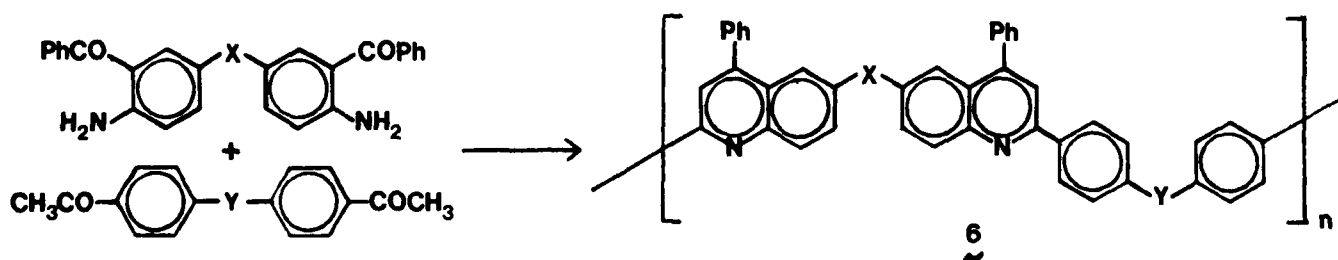
Polymers that contain pendant spiro loops attached to the polymer backbone, "cardo" polymers, give the chain enhanced rigidity.¹¹ The loops are perpendicular to the chain direction, and depending on the structural

symmetry, can produce either an ordered structure or a chain which approximates an atactic arrangement as a result of the randomness characteristic of step-reaction polymerizations.

Polymers containing the cardo structure generally possess greater rigidity, enhanced thermal stability, and excellent solubility. Most of these polymers are amorphous, primarily as a result of the bulky pendant ring and the "atactic" structure resulting from dissymmetric rings. However, polycarbonates such as the symmetrical one can be prepared in crystalline and amorphous forms. Certain cardo polymers can be crystallized with solvent or by annealing.

High heat distortion temperatures and high oxidative thermal stability also are observed. Polymers from cardo monomers having the largest value of reduced volume of the cycle to molecular weight -- for example fluorene, $K_i/M=1.58$ -- exhibit the highest heat distortion temperatures. Polymers containing cardo monomers derived from anthraquinone, however, have the best thermal stability but slightly lower heat distortion temperatures ($K_i/M=1.56$).

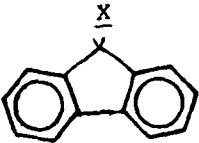
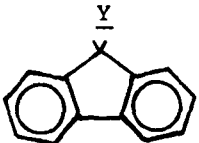
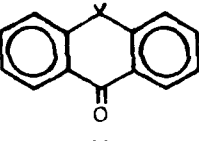
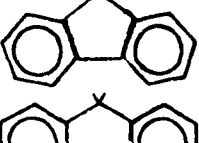
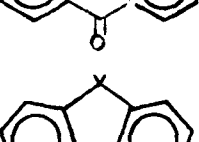

Polyquinolines containing spiro fluorene and anthraquinone units have been synthesized from the appropriate spiro-containing bismethyleneketone and bisaminoketone monomers.¹² The greater rigidity of the cardo polymers



over the non-cardo analogs ($X,Y=O$) is responsible for the higher glass transition temperatures (Table 2) yet these polymers remain soluble in common organic solvents. Glass transition temperatures were 120-140°C higher when both X and Y were cardo units, as compared to $X=Y=O$ and only

TABLE 2

Properties of Polyquinolines (6) Containing Cardo Units

| Polyquinoline 6 | | [n] | Tg (°C) | Td (°C) | E' (25°C) (dyn/cm ²) x 10 ¹⁰ |
|---|---|-------------------|---------|---------|---|
|  |  | | | | |
| a. |  | 0.58 ^a | 390 | 580 | 2.1 |
| b. |  | 0.70 ^b | 385 | 530 | 2.2 |
| c. |  | 1.30 ^b | 405 | 540 | - |
| d. |  | 0.53 ^b | 390 | 520 | 1.5 |
| e. | nil | 2.5 ^a | 420 | 570 | 1.3 |
| f. | O | 1.70 ^a | 310 | 570 | 2 |
| g. | nil | | 417 | 560 | 1.9 |
| h. | O | 0.87 ^b | 340 | 580 | 1.8 |
| i. | nil | 1.95 ^c | 380 | 580 | 1.8 |
| j. | O | 0.56 ^c | 315 | 575 | 2.5 |
| k. | nil | 0.69 ^a | 350 | 530 | 2.2 |
| | O | 0.97 | 320 | 535 | - |

a. CHCl₃b. CHCl₂-CHCl₂

c. m-cresol

45-90°C higher when only one of the oxygen units, X or Y, was replaced by a cardo group. Thus, the use temperature of polyquinolines (6) containing dicardo structures can be increased to the 400°C range. All the cardo polymers exhibited good thermal stability ($T_d > 500^\circ\text{C}$).

Rigid Rod Polyquinolines.

The series of stiff-chain polyquinolines that have been synthesized are crystalline and insoluble in common organic solvents (Table 3). The degree of crystallinity depends on the thermal history of the sample, but crystallinities of 60-80% can be achieved. The polymers are characterized by high crystalline transition temperatures ($> 500^\circ\text{C}$) and high glass transition temperatures ($> 330^\circ\text{C}$).

Although the polymers are insoluble in common organic solvents, they are soluble in strong acids (H_2SO_4 , $\text{CF}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$) and most importantly, the polymers remain soluble in the polymerization dope at the end of the polymerization. As a result, films can be cast and fibers wet spun from the polymerization medium. Solutions of rigid rod polymer 7b forms anisotropic solutions in the polymerization solvent (dicresylphosphate *m*-cresol 1:5) at about the 10 wt. percent level.

Thus, fibers spun from anisotropic solutions show orientation of the polymer chains along the direction of the fiber axis (x-ray). High dynamic storage moduli are observed for films of the polymer. The modulus is maintained even above T_g (7a), whereas a polyquinoline such as 1 ($X=\text{O}$, $R=\text{H}$, $\text{Ar}=\text{p,p}'\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4$) amorphous loses its strength at T_g (Fig 1).


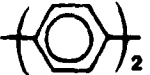



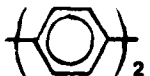
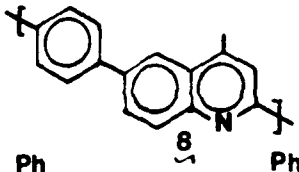
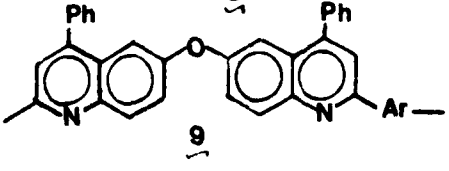

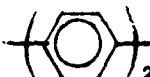

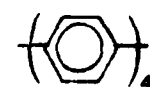
CROSSLINKING REACTIONS

Biphenylene Crosslinking

Biphenylene (10) undergoes thermolysis at $\sim 400^\circ\text{C}$ and, depending on the

TABLE 3

Rigid Rod Polyquinolines

| Polymer 7 | | [n] (dl/g) | Tg | Tm | Td (N ₂) | E' (dynes/cm ² x 10 ¹⁰) | |
|-----------|---|-------------------|-----|-----|----------------------|--|----------|
| R | Ar | | | | | 25° | Above Tg |
| a H |  | 7.0 ^a | 365 | b | 595 | 4.2 | 1.9 |
| b |  | 14.5 ^a | 330 | 500 | 577 | 3.9 | 1.8 |
| c |  | 22.0 ^a | 360 | 504 | 600 | 2.6 | 0.42 |
| d |  | i | 360 | b | 600 | c | c |
| e Ph |  | 17.0 ^a | 355 | b | 540 | 2.5 | 0.19 |
| f |  | 22 | 365 | b | 595 | 1.7 | 0.18 |
| |  | 11.6 | 380 | 580 | 610 | 4.2 | 0.36 |
| |  | | | | | | |
| a |  | 1.1 ^d | 300 | 455 | | | |
| b |  | 3.1 ^e | | 480 | | | |
| c |  | 3.5 ^a | 280 | f | 540 | 0.37 | g |
| d |  | i | 305 | f | 560 | c | c |

a. CF₃SO₃H solvent.

b. Tm > Td

c. Unable to obtain films

d. CHCl₃e. m-cresol

f. No Tm observed

g. 9.7 x 10⁷

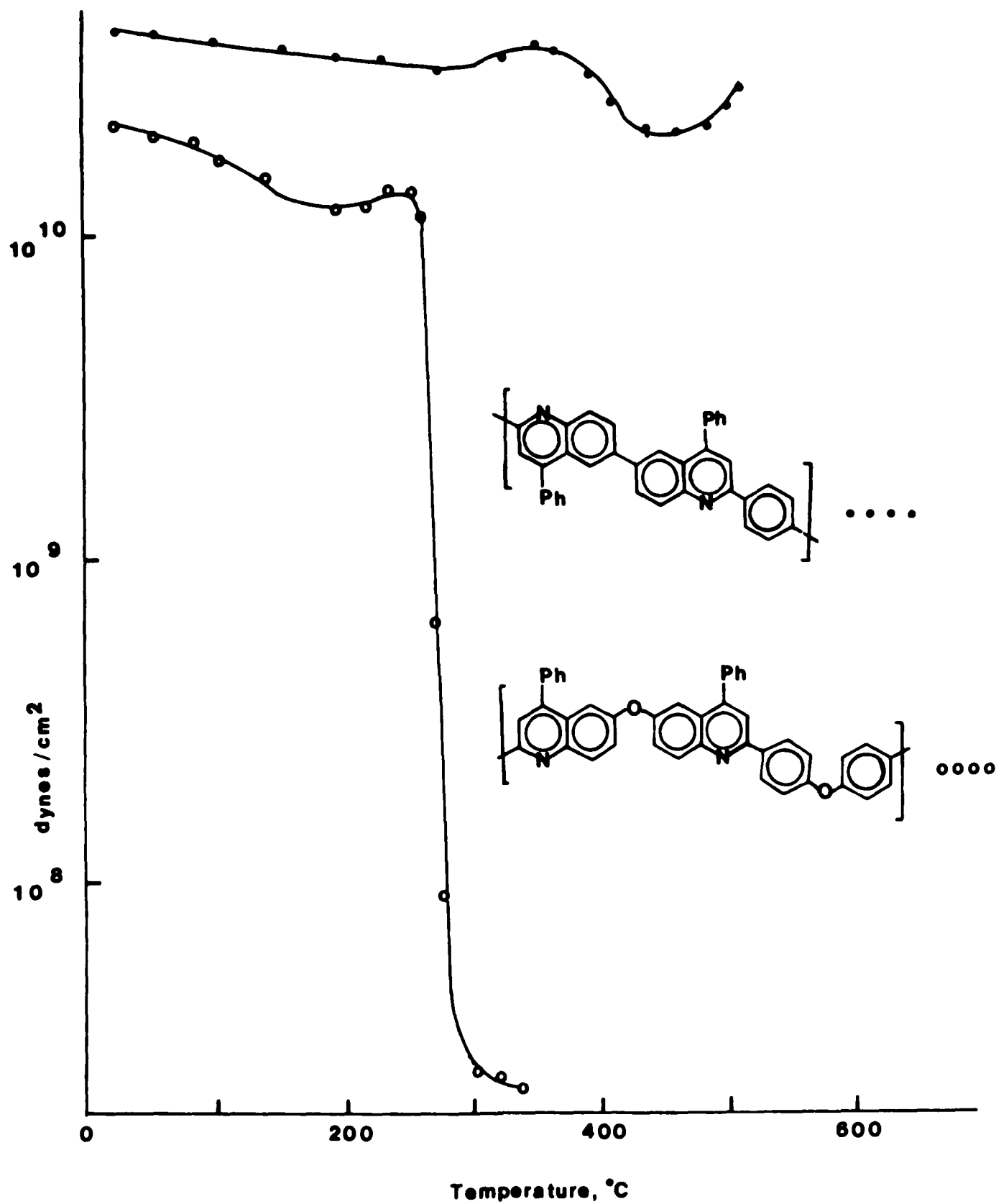
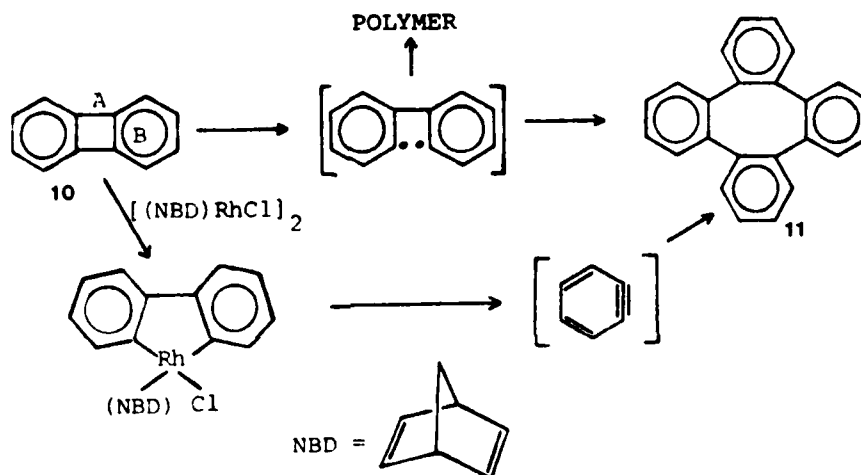


Figure 1
Thermomechanical Properties of Polyquinolines

reaction conditions, yields tetrabenzocyclooctatetraene (11), polymer, or biphenyl -- resulting from radical abstraction of hydrogen from solvent.¹³⁻¹⁵ Although the structure of the polymer was not determined, it likely contains poly-(*o*-phenylene) segments. These reports suggest a diradical as the reactive intermediate in pyrolysis. Thus, any structure formed as a result of the thermolysis of a biphenylene unit in a thermally stable polymer would be expected to maintain the high temperature structural integrity of the polymer.

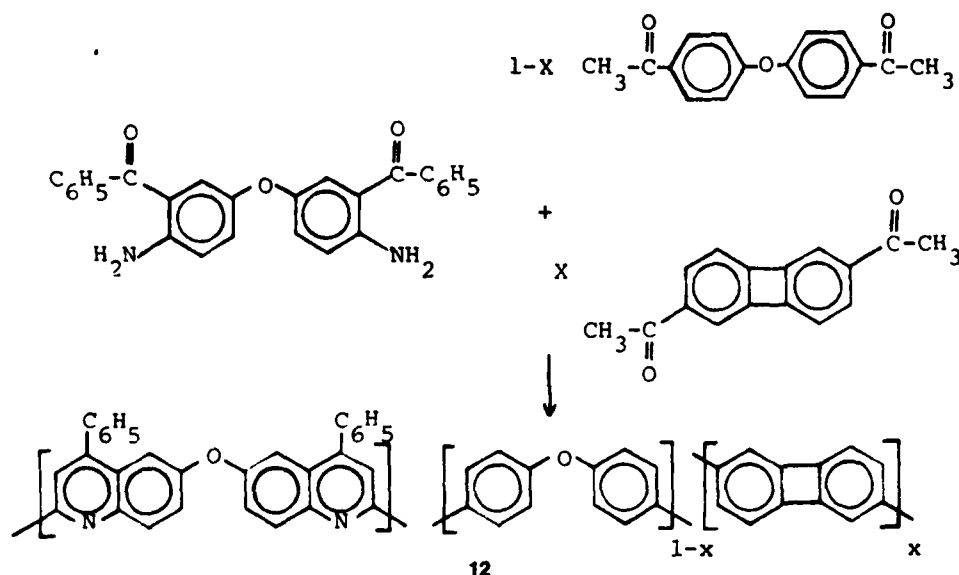


SCF-MO calculations suggest¹⁶ that biphenylene is anti-aromatic and should be somewhat chemically unstable, undergoing reactions in the anti-aromatic cyclobutadiene ring. Both calculations¹⁷ and structure determination¹⁸ show longer bond lengths between the benzo units (A) than within the benzo units (B). Calculated heats of formation for biphenylene are higher by 27.5 kcal/mol than those observed from heats of combustion;¹⁵ this difference has been attributed¹⁶ to strain energy.

Rhodium catalysts are known to open strained cyclic hydrocarbons by an oxidative addition mechanism.¹⁹ Thermolysis of biphenylene containing a catalytic amount of the rhodium catalyst at 200°C produced dibenzocycloocta-

tetraene in a 44% yield (recrystallized) and polymer. Thus, the products of the catalyzed reaction are the same as those obtained from the uncatalyzed thermolysis. By analogy to the cubane reaction,¹⁹ however, it might be expected the benzyne is the reactive intermediate. This temperature is approximately 200°C lower than that required for the uncatalyzed reaction.

The incorporation of varying portions of biphenylene in place of diphenylether into a polyquinoline was accomplished by balancing the appropriate amounts of 2,6-diacetylbiphenylene in place of 4,4'-diacetyldiphenylether under standard polymerization conditions.²⁰⁻²²



| | | Tg |
|----|-----------|-----|
| a. | x = 1.0 | 297 |
| b. | x = 0.5 | 270 |
| c. | x = 0.25 | 258 |
| d. | x = 0.05 | 240 |
| e. | x = 0.025 | 232 |
| f. | x = 0 | 266 |

The glass transition temperature of the parent polyquinoline containing all biphenylene units was lowered by increasing the content of diphenyl-ether units; copolymer 12c has a lower T_g than the homopolymer 12f. A reaction exotherm attributed to the opening of the biphenylene ring was observed above 300°C. The time required for curing depended on the curing temperature (340-380°C), as well as the biphenylene content of the polymer. The onset of the exotherm for crosslinking increased with an increasing biphenylene amount and paralleled the increase in T_g . (Fig 2).

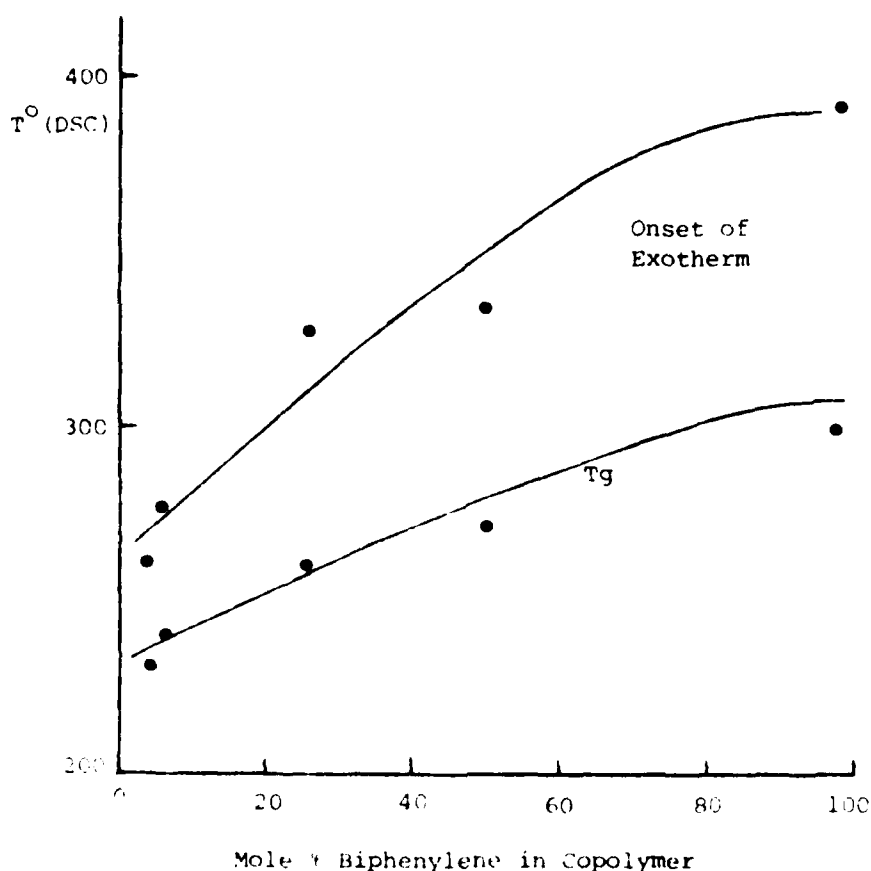


Fig. 2. Dependence of Exotherm Onset on Biphenylene Content

Since biphenylene underwent a rhodium catalyzed ring-opening at much lower temperatures to afford the same products as obtained from the uncatalyzed reaction, curing was carried out on polymer samples containing

catalytic amounts of norbornadiene-chlororhodium(I) dimer. Generally, lower temperatures and shorter reaction times were used to effect the same crosslinking reaction. The thermal mechanical analysis of polymers 12c and 12d showed that curing at 380°C for 1 hour was sufficient to erase the glass transition temperature. In polymer 12e, a very high transition temperature is observed after curing at 380°C for 1 hour. At 380°C, the effect of curing time on the glass transition temperature of this polymer (12e) containing only 2.5% biphenylene units, is to increase Tg. Rhodium catalysis does this more effectively (Fig. 3). At a curing time of 3 min, the difference in the rhodium cures and the catalyzed curing is most pronounced with polymer 12c containing 25% biphenylene. Generally, curing was accompanied by insolubility in all solvents, an increase in Tg and finally disappearance of Tg.

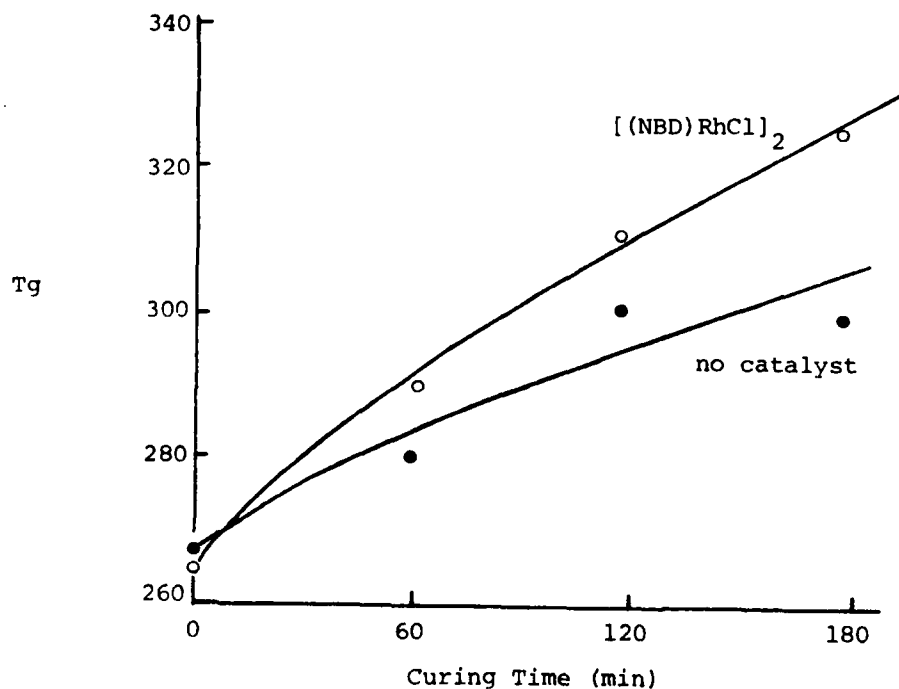


Fig. 3. Copolymer 12e Curing

The dynamic mechanical properties of uncured and cured films of poly-quinolines 12a-f were obtained from room temperature up to 380°C. Under the mild tensile stresses required, the mechanical performance of films is relatively constant up to the glass transition temperature.

The dynamic moduli of the cured polymers at low temperature (25-250°C) are, as expected, higher than those of the uncured polymers. The glass transition temperatures after curing are 30-60°C higher than the uncured samples, as measured by the moduli. More importantly, the moduli of the cured polymers above T_g are much higher than those of the homopolymer, 12f, and are a function of the percent biphenylene in the copolymer (Fig 4). Even a low biphenylene incorporation (2.5%, 12e) is sufficient to raise the value from 2.4×10^7 to 3.8×10^8 dyn/cm² (Fig 5).

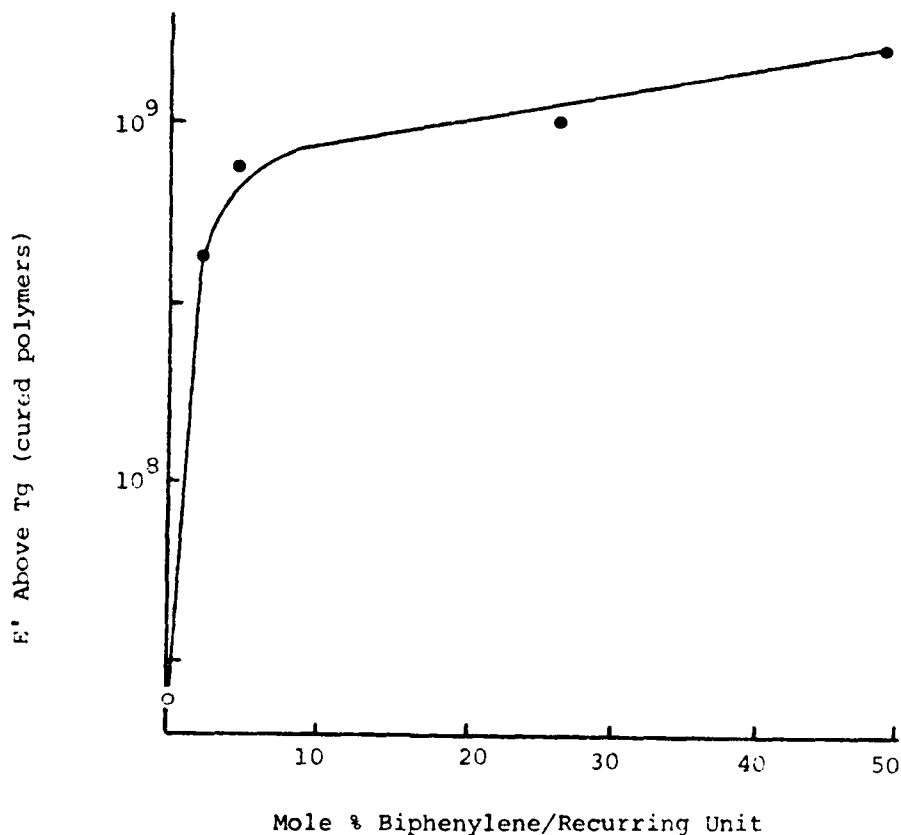


Fig. 4. E' of 12e (cured) Above T_g

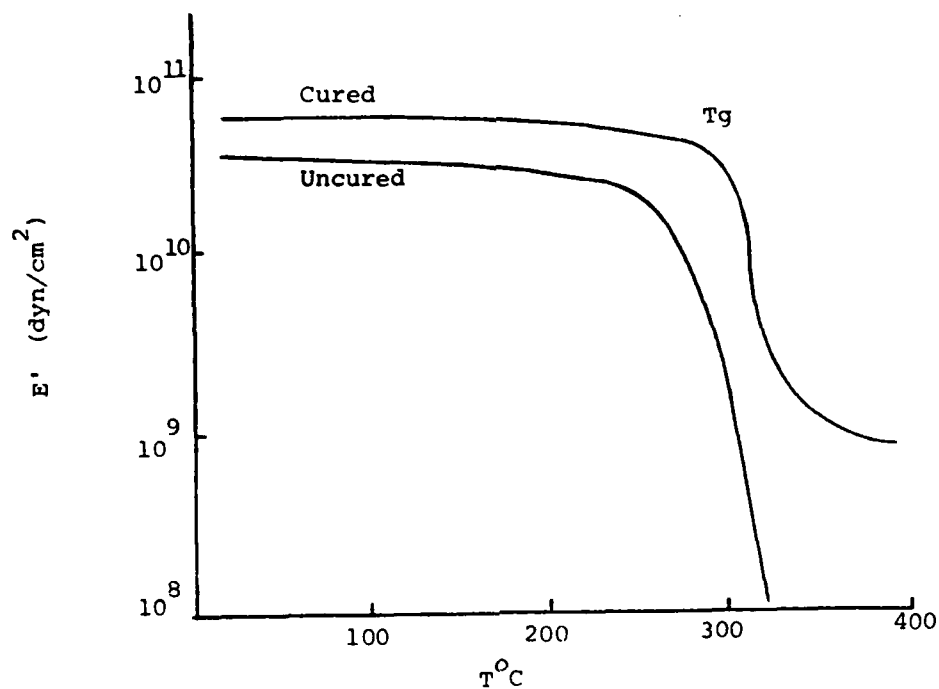


Fig. 5. E' of Copolymer 12 vs Temperature

Finally, it is instructive to compare the dynamic storage moduli (E') above T_g for polymer 12 cured with and without catalyst as a function of curing time (Fig 6). As expected, the catalytic effect is reflected by the generation of higher moduli for the low curing times.

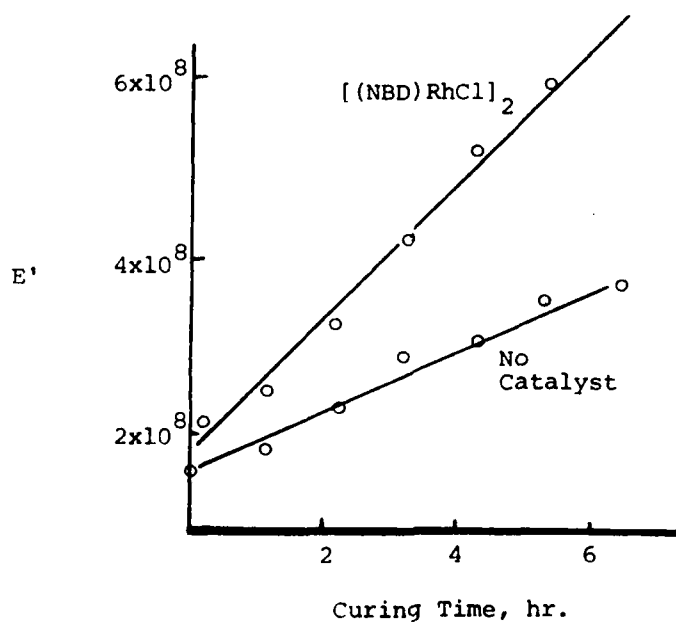
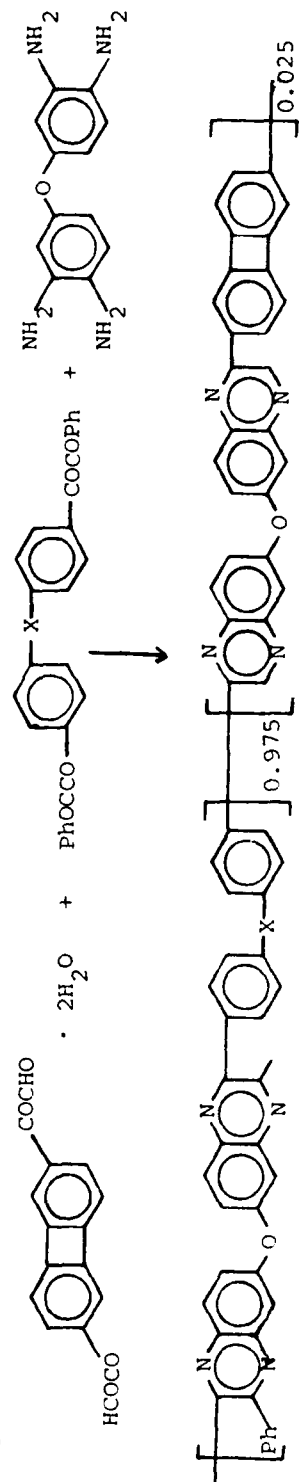
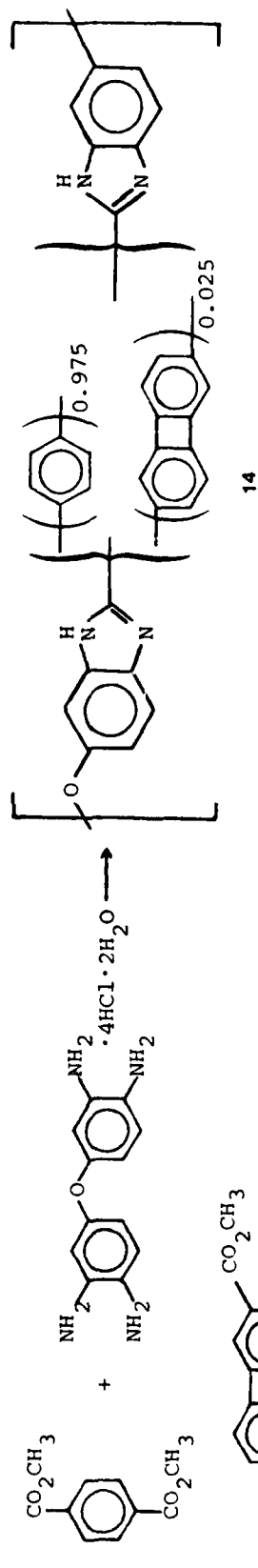
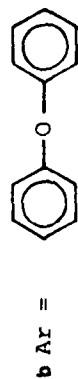
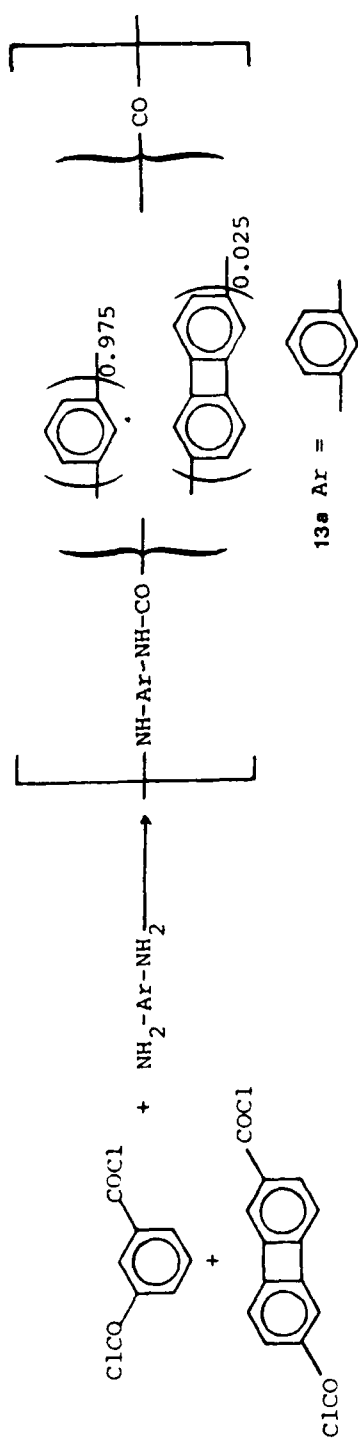


Fig. 6. E' Above T_g vs Curing Time, Copolymer 12

The thermal gravimetric analysis of cured polymer samples and of the parent polymer (12f) that does not contain the biphenylene units showed breaks at the same temperatures, and under nitrogen, suffered the same weight loss up to 800°C. This provides some evidence that in the curing reaction, stable crosslinks are indeed formed.

This method of crosslinking polyquinolines is applicable to crosslinking a wide variety of thermally stable polymers, including polyamides, polybenzimidazoles, and polyquinoxalines.²³ Aromatic polyamides (13) have been synthesized by substituting biphenylene-2,6-dicarboxylic acid chloride (2.5 mole percent) for isophthaloyl chloride in polymerization with two different amines, *m*-phenylenediamine and 4,4'-diaminodiphenylether in *N*'-methylpyrrolidone with propylene oxide as an acid acceptor.^{24,25} A polyaromatic benzimidazole (14) was synthesized by substituting dimethyl biphenylene-2,6-dicarboxylate (2.5%) for dimethyl terephthalate in polymerization with 3,3'-4,4'-tetraaminodiphenylether tetrahydrochloride in polyphosphoric acid at 200°C. Polyquinoxalines (15) were synthesized by substituting 2,6-diglyoxalylbiphenylene (2.5%) for two dibenzils in polymerization with 3,3'-4,4'-tetraaminodiphenylether in a 1:1 mixture of *m*-cresol-xylene at ambient temperature.

The DSC and TMA cells were used to cure samples of polymer film. After curing, the Tg of the samples were recorded as well as their thermal behavior up to 400°C. In all cases the magnitude of the deflection at Tg in the cured samples was sharply reduced compared to those recorded during the heating period up to the curing temperature. The samples were completely insoluble after curing 3 h at 380°C; however, the DSC trace still exhibited an intense exothermic peak after curing.



The dynamic mechanical properties of uncured and cured films of polyamides 13 and polyquinoxalines 15 were obtained from room temperature to 450°C.

In the case of polybenzimidazole 14 no Tg was visible by DSC at the highest sensitivity of the instrument. Modulus measurements were not made since good films could not be obtained as a result of the poor solubility of the polymer in the common organic solvents. Thus, the crosslinking could be followed only by its solubility before and after curing. The uncured polybenzimidazole was soluble in concentrated sulfuric acid and partially soluble in DMAC, DMSO and DMF. After curing 3 h at 380°C the polymer sample was completely insoluble in DMSO, DMF and DMAC, but it required 6 h curing to achieve insolubility in concentrated sulfuric acid. The Young's modulus of films are relatively constant up to the glass transition temperature both for polyamides and polyquinoxalines. A major relaxation occurs in the glass transition interval, resulting in a decrease of E' from the order of 10^{10} to $10^7 - 10^8$ dynes/cm².

In the case of polyamide 13a the E' above Tg was found to have a value of 2.8×10^9 and the polymer could not be cured at temperatures higher than 340°C because broken films resulted. These facts provide some evidence that this polymer maintains a high degree of crystallinity even after the introduction of biphenylene in the chain. Correlations between DSC, TMA and the maximum in the loss modulus (E'') were relatively good for all the polymers. The effect of curing on the dynamic storage moduli of polyquinoxaline 15b is shown in Figure 7. The sharp decrease in the dynamic storage moduli representing the Tg of polyquinoxalines void of biphenylene units is progressively shifted towards higher temperatures by heating the films at 400°C in an inert atmosphere. This effect was attributed to

pyrolytic crosslinking. However, introduction of biphenylene in the polymer chain allows the use of lower curing temperatures (350°C vs 400°C) and lower curing times (4 h vs 8 h) to give a material that undergoes a maximum in loss modulus at higher temperatures, and has a higher modulus, especially above the T_g (Fig 7). It is interesting to note also that within the two

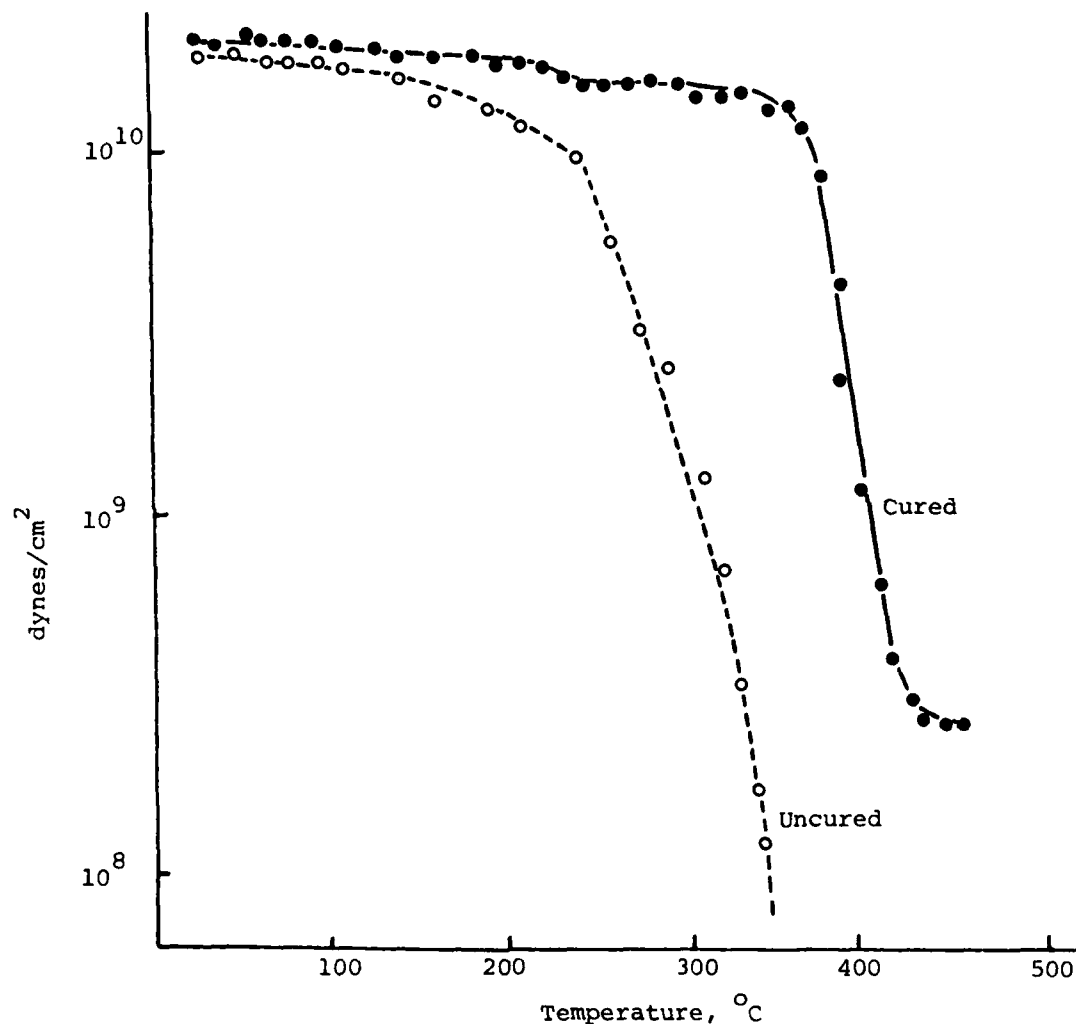


Fig. 7. E' of Copolymer 15b vs Temperature

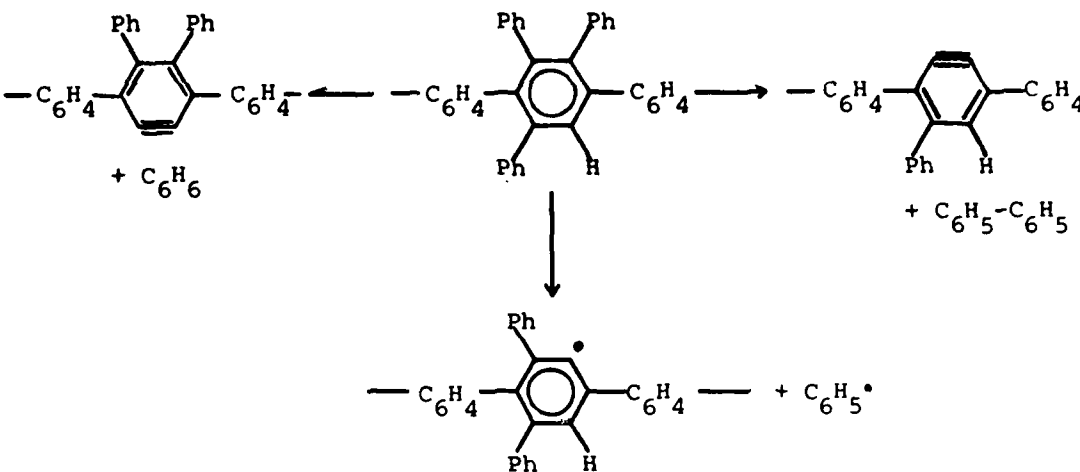
polyquinoxalines 15a and 15b studied here, the crosslinking does not have the same efficiency. In fact, in polymer 15b a large increase in the T_g (365° vs 270°C) is observed by TMA after curing for 1 h at 380°C, and this

is in accordance with the very high temperature at which the maximum in the loss modulus is observed after curing film samples (327° vs 270°C) (Fig 7). Such a high increase in the T_g is not observed in polymer 15a. There is no obvious explanation for this difference, but it is apparent that with polymers containing such a small percentage of biphenylene units in the chain, the crosslinking probably occurs through a series of radical abstraction and coupling reactions, rather than tetrabenzocyclooctatetraene formation (dimerization). The radical reaction appears to be more favored in polymer 15b containing biphenyl than in polymer 15a containing diphenylether.

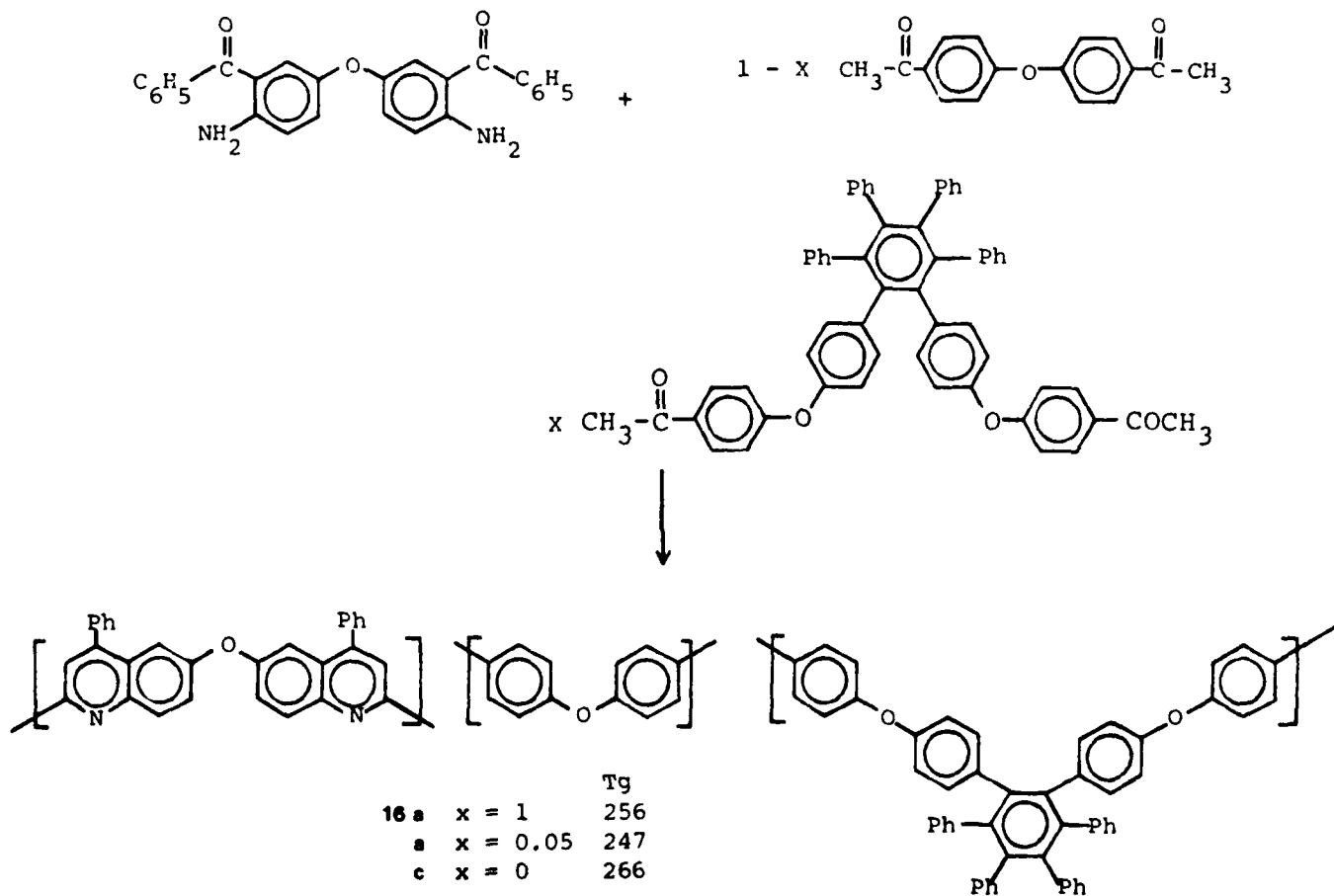
Hexaphenylbenzene Crosslinking.

Hexaphenylbenzene decomposes rapidly at 450°C, a temperature well below that of biphenyl (550°C).²⁶ It has been observed that phenylated polyphenylenes decompose with the loss of benzene and biphenyl at 550°C, but that free radicals are produced at 350°C in these polymers, and crosslinking does occur. The mechanism of these decompositions and crosslinking is unknown, but in the case of the phenylated polyphenylenes, the main chain does not undergo appreciable scission; instead, the pendent phenyl groups are lost. Polyphenylenes that do not contain the pendent phenyl groups do not lose benzene or biphenyl at 550°C, and do not crosslink at temperatures below 500°C.²⁷⁻²⁹ The homolytic bond breaking to form the free radical species and/or the formation of benzyne could explain these results. Presumably the reaction of a hexaphenylated benzene in a polymer backbone would take place at lower temperatures.

The copolymerization of the diacetyl monomer containing a hexaphenylbenzene arrangement and 4,4'-diacetyldiphenylether with 3,3'-dibenzoylbenzidine gave polymers containing the desired perphenylated phenylene unit.³⁰



The glass transition temperature of uncured samples of polymer containing 5% of the phenylated phenylene moiety was only slightly below the analogous polyquinoline homopolymer (255° vs 247°C). The cured polymers showed an increase or disappearance of the Tg, complete insolubility in all solvents, and higher moduli, particularly at temperatures above the original Tg.



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APPENDIX I

List of Publications

ARO Support 1977-1979

J. Garapon, W.H. Beever and J.K. Stille, Polymer Preprints, 18(1), 138 (1977); "Polyquinolines: A Class of Rigid Chain Polymers".

J.K. Stille, J. Wolfe, S. Norris, Y. Imai, E.F. Johnson, T. Katto and M. Kurihara, "Polymers Containing Quinoline and Anthrazoline Units in the Main Chain" in "Advances in the Chemistry of Thermally Stable Polymers", Warszawa, 1977, p 9.

J. Garapon and J.K. Stille, Macromolecules, 10, 627 (1977); "Biphenylene as Cross-Linking Sites for Polyquinolines".

C. Chiriac and J.K. Stille, Macromolecules, 10, 710 (1977); "Aromatic Polyamides by a Direct Polycondensation Reaction".

C. Chiriac and J.K. Stille, Macromolecules, 10, 712 (1977); "Polyaramides Containing Sulfone Ether Units".

A. Recca, J. Garapon and J.K. Stille, Macromolecules, 10, 1344 (1977); "Biphenylene as a Cross-Linking Site. Curing Conditions, Glass Transition Temperatures and Moduli of High Molecular Weight Polyquinolines Containing Biphenylene Units in the Chain".

R.T. Kohl, T. Katto, J.N. Braham and J.K. Stille, Macromolecules, 11, 340 (1978); "Diels-Alder Reactions of Phenyl-Substituted 2-Pyrones: Direction of Addition with Phenylacetylene".

J.N. Braham, T. Hodgins, T. Katto, R.T. Kohl and J. K. Stille, Macromolecules, 11, 343 (1978); "Polyphenylenes via Bis(2-pyrones) and Diethynylbenzenes. The Effect of *m*- and *p*-Phenylene Units in the Chain".

A. Recca and J.K. Stille, Macromolecules, 11, 479 (1978); "Biphenylene as a Cross-Linking Site in Theramilly Stable Polymers".

J.K. Stille, Pure and Appl. Chem., 50, 273-80 (1978); "Polyquinolines: Versatile Aromatics with Diverse Properties".

W.H. Beever and J.K. Stille, Journal of Polymer Science: Polymer Symposium, 65, 41-53 (1978); "Polyquinolines: A Class of Rigid-Chain Polymers".

R.M. Harris, S. Padaki, P. Sybert and J.K. Stille, Polymer Preprints, 19(2), 7 (1978); "Polyquinolines: Rigid Rod Polymers and Chains Containing Pendent Spiro Units".

G.L. Baker and J.K. Stille, Macromolecules, 12, 369 (1979); "Hexaarylbenzene Units as Cross-Linking Sites for Polyquinolines".

W.H. Beever and J.K. Stille, Macromolecules, 12, 1033 (1979); "The Synthesis and Thermal Properties of Aromatic Polymers Containing 3,6-Quinoline Units in the Main Chain".

APPENDIX 2

List of Participating Scientific Personnel

NAME

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Dr. A. Recca

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Mr. S. Padaki

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Mr. J. Droske